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Citation: Appl. Phys. Lett. **85**, 534 (2004); doi: 10.1063/1.1771451
View online: http://dx.doi.org/10.1063/1.1771451
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HTML ABSTRACT + LINKS

High-performance photorefractive polymers sensitized by cadmium selenide nanoparticles

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(Received 9 February 2004; accepted 12 May 2004)

We report on efficient and fast hybrid photorefractive polymer sensitized with cadmium selenide (CdSe) quantum dots. The surface of the quantum dots was treated with 4-methylbenzenethiol. This surfactant is responsible for efficient photoinduced charge generation in the composite, leading to fast grating build-up times of 100 ms and below. Overmodulation of the diffraction efficiency was observed at an applied field of 60 V/μm. © *2004 American Institute of Physics*.
[DOI: 10.1063/1.1771451]

In recent years, the number of potential applications for nanoparticles in technology has been growing considerably, mainly motivated by the ability to fine tune their optical and electrical properties by controlling their size.[1] Quantum confinement effects are used to confer properties to the nanoparticles that are markedly different from those of the bulk. For instance, spherical semiconductor nanoparticles (or quantum dots) integrated in organic semiconductors have been used recently in electroluminescent devices,[2,3] photovoltaic cells,[4] and quantum dot lasers.[5] Here, semiconductor nanoparticles are used as sensitizers in efficient photorefractive (PR) polymers.

PR materials have numerous potential applications in real-time optical processing because they provide a medium for the recording of reversible and nonlocal volume holograms. The first step in the generation of a PR hologram involves the photogeneration of charge carriers. This is generally achieved in traditional polymers by doping the material with a small amount of organic molecules that form a charge-transfer (CT) complex with the semiconducting matrix, providing sensitivity in the visible and near infrared.[6,7] PR polymers can also be sensitized with quantum dots (QDs) of semiconductors, such as CdS,[8] CdSe,[9,10] PbS,[11] or HgS.[11] However, to date, the performance of such materials in terms of diffraction efficiency and response time was found to be inferior to that of materials sensitized with organic molecules. The slower dynamic response can be attributed to the surfactant coated on the surface of the QD that provides for solubility but simultaneously reduces the electron transfer efficiency[12] during the photogeneration of carriers. In this letter, we report on a PR composite sensitized by cadmium selenide (CdSe) QDs coated with a thin surfactant that enables efficient photoinduced charge generation in the mixture and leads to response times of 100 ms and below, combined with a large dynamic range.

The nanoparticles were synthesized by the reverse micelle method.[13] The size of the nanoparticles could be controlled by changing the surfactant-to-water ratio W, as well as the reaction time. This allows the absorption edge to be tuned from 650 nm to 500 nm by decreasing their average size. In comparison, the absorption edge of bulk CdSe is 712 nm. The surface of the CdSe nanoparticles was treated with 4-methylbenzenethiol. This surface treatment provides good chemical stability and simultaneously ensures good solubility in the common solvents used to mix the different components necessary to produce PR polymers. To synthesize the CdSe nanoparticles, a surfactant-to-water ratio of $W=11.1$ was used to provide sensitivity at 633 nm.

The performance of the QDs as sensitizers was investigated by incorporating them into a polymer composite, referred to as **QD**, with the following composition: PVK/4-homopiperidino-benzylidenemalononitrile(7DCST)/3-(N,N-di-n-butylaniline-4-yl)-1-dicyanomethylidene-2cyclohexene (DBDC)/benzylbuthylphtalate(BBP)/CdSe (49/25/15/10/1 wt.%). PVK provided the *p*-type semiconducting matrix, mixtures of 7DCST and DBDC were used as chromophores to confer orientational birefringence and good phase stability to the composite, and BBP was a plasticizer that reduced the glass transition temperature to ensure rotational mobility of the chromophores. For reference, a composite referred to as **R**, without extrinsic sensitizer, and composition: PVK/7DCST/DBDC/BBP (50/25/15/10 wt.%) was also prepared. Composites **QD** and **R** were sandwiched between two indium-tin coated coated glass slides leading to samples of type **QD** and **R**, respectively. The absorption coefficient (α) at 633 nm of 105 μm thick samples was 143 cm^{-1} and 6 cm^{-1} in **QD** and **R** respectively. Differential scanning calorimetry experiments conducted on composites **QD** and **R** yielded a broad range of glass temperatures between 20 and 40°C. The ability of the chromophores to reorient in the composite was further confirmed using a transient ellipsometry technique.[14] Samples of a composite referred as **PM**, with composition PVK/BBP/CdSe (70/29/1 wt.%), were prepared to provide a comparison with the photoconductive properties of samples **QD** and to isolate the contribution of the nanoparticles to the photogeneration of carriers from the possible influence of the chromophore. The absorption coefficient of 105 μm thick **PM** samples, at 633 nm, was 63 cm^{-1}. Surprisingly, the absorption of **QD** was different from that expected from the linear superposition of the ab-

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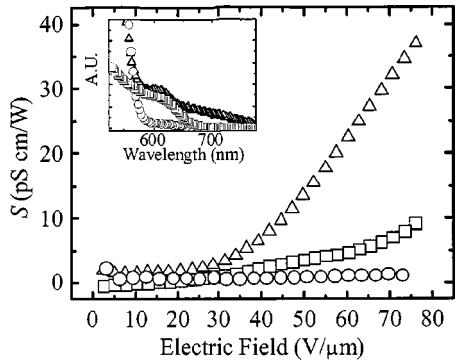

FIG. 1. Field dependent photosensitivity at 633 nm in samples **QD** (triangles), **R** (circles), and **PM** (squares). Inset: Visible spectrum of thin films of samples **QD** (triangles), **R** (circles), and **PM** (squares).

sorption of composites **R** and **PM**, suggesting the possible formation of a CT state between the nanoparticles and the chromophores since no evident CT states where observed with the matrix itself. As shown in the inset of Fig. 1, the formation of a broad redshifted band was confirmed in thin films of the composite **QD**, and led to a significant increase of the photoconductivity σ_{ph}. As shown in Fig. 1, the larger photosensitive response, defined as $S=\sigma_{ph}/I$, of samples **QD**, as compared with that of **PM**, confirms that in the presence of the chromophores the photogeneration of carriers is significantly enhanced.

The photorefractive properties were characterized by four-wave mixing and two-beam coupling experiments. The tilted geometry configuration was used, in which two 633 nm writing beams are incident on the sample with an interbeam angle of 20.5° in air and the surface sample normal is tilted 60° with respect to the writing beam bisector. Transient four-wave mixing experiments were carried out to evaluate the effect of the improved photosensitivity in samples **QD**. The diffracted power transients were fitted using Kogelnik's thick-grating equation,[15] where the time-dependent index modulation was approximated by $\Delta n(t) \propto 1-m\exp[-t/\tau_1]-(1-m)\exp[-t/\tau_2]$. As shown in the inset of Fig. 2, the dominant time constants (τ_1) in samples **QD** were consistently smaller by more than an order of magnitude with respect to the ones obtained in samples **R**. Typical

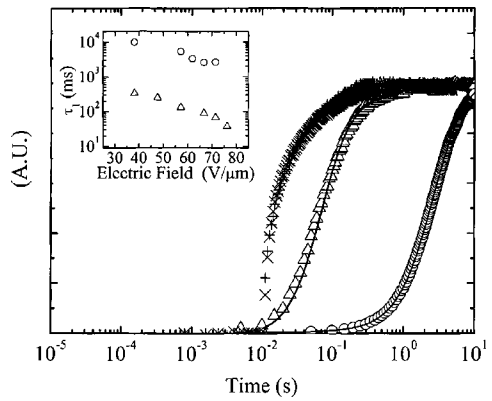

FIG. 2. Temporal evolution of the diffraction efficiency in sample **QD** (triangles) and sample **R** (circles) at 66.7 V/μm and temporal evolution of the birefringent response in samples **QD** (+ symbols) and in sample **R** ($\times$ symbols) at 57 V/μm; solid lines are fits to a sine-squared weighted biexponential temporal evolution. Inset shows the field dependence of the fast time constant, τ_1, of the photorefractive grating build-up in samples **QD** (triangles) and **R** (circles).

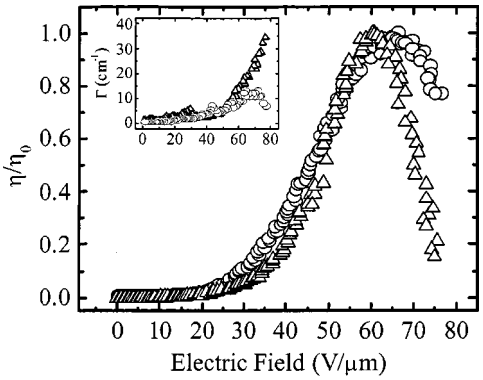

FIG. 3. Field dependence of the normalized steady-state diffraction efficiency measured in samples **QD** (triangles) and **R** (circles). Inset shows the field dependent gain coefficients measured in samples **QD** (triangles) and **R** (circles).

weight factors, m, were around 0.7 and 0.6 for samples **QD** and **R**, respectively. For instance, at 67 V/μm, τ_1 in sample **QD** was 87 ms with $m=0.69$ whereas in sample **R**, τ_1 was 2.7 s with $m=0.56$. As shown in Fig. 2, the dynamics of the chromophore reorientation was the same in both samples and faster than the grating build-up times. Although τ_1 cannot be directly correlated to the space-charge field rise time since the dispersive nature of chromophore reorientation affect the dynamics of formation of the space-charge field,[16] for our samples, provided a nearly identical orientational dynamics, it is reasonable to ascribe differences in the values of τ_1 to a difference in the rate of formation of the space-charge field (τ_{sc}^{-1}). Since τ_{sc}^{-1} is proportional to the rate of absorption per unit length (αI), differences in absorption can be compensated for by the proper normalization of the initial build-up rate by αI. For times $t<\tau_1 \ll \tau_2$, the first-order approximation of $\Delta n(t)$ yields an initial build-up rate proportional to m/τ_1. At 67 V/μm, the value of the normalized build-up rate is 0.055 cm^3/J in samples **QD** and 0.035 cm^3/J in **R**. Therefore, differences in the formation rates must be attributed to the contribution of the nanoparticles to the photogeneration of carriers. With the high value for the ionization potential of CdSe (6.7 eV), the optical excitation of the nanoparticles is likely to lead to the injection of a hole into the chromophore and/or matrix which have both ionization potentials of 5.9 eV.

The steady-state PR properties of samples **QD** and **R** are shown in Fig. 3. In both types of samples, overmodulation of the diffraction efficiency was observed at around 60 V/μm. The maximum external diffraction efficiency in samples **QD**, around 20%, was limited by absorption and scattering. Due to the photosensitive response in samples **R**, similar diffraction efficiency to samples **QD** is expected provided their chromophore content and that steady state has been reached. As show in the inset of Fig. 3, the gain coefficients at low electric fields are also similar in both types of samples and start to differ for fields above 50 V/μm where the contribution of the QDs to the photogeneration and redistribution of carriers start to be significant.

In summary, we have developed a hybrid PR polymer with properties comparable to those of composites sensitized with organic molecules. It was shown that the use of 4-methylbenzenethiol as a surfactant enables an efficient photogeneration of carriers in the bulk that leads to hybrid PR composites with unprecedented response times and large

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dynamic range. With the wide variety of semiconductor QDs with different band gaps, PR polymers can potentially be sensitized over a broad spectrum, including at wavelengths for telecommunications (1300–1600 nm).

This work was supported by the NSF through an ECS and a CAREER grant for one of the authors (B.K.), and AFOSR. Another author (C.F.-H.) thanks CONACyT for scholarship No. 133376.

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